

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 104 800 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

06.06.2001 Bulletin 2001/23

(21) Application number: **00310763.8**

(22) Date of filing: **04.12.2000**

(51) Int Cl.⁷: **C10M 163/00**, C10M 141/12

// (C10M141/12, 129:44,
135:30, 135:10, 139:00, 137:10,
135:18, 133:12, 129:10),
(C10M163/00, 159:22, 159:24,
139:00, 135:18, 137:10, 133:12,
129:10),
(C10N10/04, 30:04, 30:10,
40:25)

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **02.12.1999 JP 34312899**

(71) Applicant: **ORONITE JAPAN LIMITED**
Minatu-ku, Tokyo (JP)

(72) Inventors:

- **Andoh, Hiroki**
Haibara-gun, Shizuoka (JP)

• **Fujita, Hirokazu**

Haibara-gun, Shizuoka (JP)

• **Kozuka, Mitsuaki**

Haibara-gun, Shizuoka (JP)

• **Nakazato, Morikuni**

Ogasa-gun (JP)

(74) Representative: **Nash, David Allan et al**

Haseltine Lake & Co.,
Imperial House, 15-19 Kingsway
London WC2B 6UD (GB)

(54) **Lubricating oil composition for gas engines**

(57) The present invention relates to a lubricating oil composition for internal combustion engines, particularly gas engines utilizing gaseous fuel, such as natural

gas or liquid propane gas. The lubricating oil composition of the present invention is useful in a method of improving the detergency and oxidation stability at elevated temperatures of gas engines.

EP 1 104 800 A2

Description

[0001] The present invention relates to a lubricating oil composition for internal combustion engines, particularly for gas engines using gaseous fuel such as natural gas or liquid propane gas. The lubricating oil composition of the present invention is useful in a method of improving the detergency and oxidation stability at elevated temperatures of gas engines.

BACKGROUND OF THE INVENTION

[0002] Electric generators and co-generation systems are widely utilized in retail stores or shops and small-scale factories. A variety of engine systems for in-house electric generators and co-generation systems may be utilized. In particular, gas engines using gaseous fuel such as natural gas or liquid propane gas (LPG) are widely used because gas engines produce low noise and low atmospheric pollution.

[0003] Generally, gas engines are designed to burn gaseous fuel at a temperature higher than that used in other internal combustion engines. Furthermore, gas engines have a small-size oil pan. Therefore, gas engines are apt to generate an increased amount of nitrogen oxides (NO_x), and engine oils employed in gas engines are apt to deteriorate in a relatively short period of time. For these reasons, gas engine lubricating oils need high detergency at elevated temperatures and also oxidation stability at elevated temperatures. It is further noted that gas engines are generally used continuously for long periods of time before oil changes occur.

[0004] It is known that detergency of engine oils at elevated temperatures can be increased by utilizing a metal-containing detergent such as calcium sulfonate, calcium phenate, or calcium salicylate. It is also known that the oxidation stability of engine oil not only at elevated temperatures but also at low temperatures can be attained by utilizing zinc dialkyldithiophosphate.

[0005] Therefore, lubricating oil compositions for gas engines have high contents of metal-containing detergent and zinc dialkyldithiophosphate.

[0006] However, gas engines are generally equipped with exhaust gas processors containing a three-way catalyst to trap nitrogen oxides. Alkali metal- or alkaline earth metal-containing detergents and phosphorus in zinc dialkyldithiophosphates are known to poison the catalyst. So while it is necessary to have enough metal-containing detergent and zinc dialkyldithiophosphate for sufficient detergency and oxidation stability at elevated temperatures, their amounts should not poison the catalyst. Accordingly, it is required to reduce the amounts of metal-containing detergents and zinc dialkyldithiophosphates in lubricating oil compositions for gas engines.

[0007] The performance requirements for lubricating oil compositions for gas engines have been reported.

[0008] Japanese Patent Provisional Publication No.7-126,681 describes a lubricating oil composition preferably employable for gas engines of the heat pump type, which comprises in a base oil, a polyalkenylsuccinimide and/or its borate derivative, a diarylamine, and a hindered phenol. The lubricating oil composition has excellent oxidation resistance to nitrogen oxides.

[0009] Japanese Patent Provisional Publication No.7-258,678 describes a lubricating oil composition for gas engines which comprises in a base oil (mineral oil, synthetic oil, or their mixture), an alkaline earth metal salicylate, a bis type high molecular weight alkenylsuccinimide or its derivative, zinc dialkyldithiophosphate, and a high molecular weight hindered phenol.

[0010] Japanese Patent Provisional Publication No.10-219,266 describes a lubricating oil composition preferably employable for gas engines of the heat pump type, which comprises in a base oil, a metal salicylate, an amine oxidation inhibitor, a hindered phenol oxidation inhibitor, and a polyalkenylsuccinimide and/or its derivative.

[0011] EP 72,519 A2 describes a lubricating oil composition appropriately employable for stationary gas engines, which comprises a calcium overbased acidic material, a magnesium overbased acidic material, and a combination of an alkylene-coupled hindered phenol antioxidant and an antioxidant other than an alkylene-coupled hindered phenol antioxidant. This publication further describes addition of a borated dispersant to the oil composition and addition of a dialkyldithiophosphate of a metal salt to the oil composition.

[0012] U.S. Patent No. 5,629,272, issued May 13, 1997, to Nakazato et al. describes an engine oil composition which comprises a metal-containing detergent, zinc dithiophosphate, and a boron-containing ashless dispersant dissolved or dispersed in a base oil; characterized by further containing an antiwear agent having an aliphatic amide compound and either a dithiocarbamate compound or an ester derived from a fatty acid and boric acid. The engine oil composition described provides excellent characteristics in antiwear, especially in reducing wear of the valve train system of internal combustion engines.

[0013] Some of the lubricating oil compositions described in the above-identified publications do not reduce the catalyst poisoning of three way catalyst in exhaust gas processors. Others do not satisfy the requirements of the high temperature detergency and high temperature oxidation inhibition of a gas-engine lubricating oil composition. Therefore, there is a need to have a lubricating oil composition having good detergency at elevated temperatures as well as

good oxidation stability at elevated temperatures on one hand and, on the other hand, having levels of metal-containing detergents and zinc dialkyldithiophosphates so as to prevent catalyst poisoning.

SUMMARY OF THE INVENTION

[0014] The present invention relates to a lubricating oil composition for internal combustion engines, particularly gas engines utilizing gaseous fuel, such as natural gas or liquid propane gas. The lubricating oil composition of the present invention is useful in a method of improving the detergency and oxidation stability at elevated temperatures of gas engines.

[0015] The lubricating oil composition of the present invention comprises:

- a) a major amount of a base oil of lubricating viscosity,
- b) a metal-containing detergent in an amount of 0.1 to 1 wt % in terms of its sulfated ash content,
- c) a boron-containing alkenyl- or alkylsuccinimide in an amount of 1.0 to 15 wt % in terms of its active ingredient,
- d) a zinc dialkyldithiophosphate in an amount of 0.01 to 0.1 wt % in terms of its phosphorus content,
- e) an oxidation inhibitor in an amount of 0.1 to 5 wt % in terms of its active ingredient, and
- f) an ashless dithiocarbamate in an amount of 0.1 to 5 wt % in terms of its active ingredient.

[0016] In one embodiment, the lubricating oil composition of the present invention has a sulfated ash content in an amount of 0.1 to 1 wt % and a phosphorus content in an amount of 0.01 to 0.1 wt %.

[0017] In another embodiment, the lubricating oil composition of the present invention has a boron content in an amount of 0.01 to 0.2 wt %.

[0018] In still another embodiment, the present invention provides for a method of producing the gas engine lubricating oil composition of the present invention by blending a mixture of a major amount of a base oil of lubricating viscosity and an effective amount of a metal-containing detergent, a boron-containing alkenyl- or alkylsuccinimide, a zinc dialkyldithiophosphate, an oxidation inhibitor, and an ashless dithiocarbamate to improve detergency and oxidation stability at elevated temperatures.

[0019] In still yet another embodiment, the present invention relates to the use of a metal-containing detergent, a boron-containing alkenyl- or alkylsuccinimide, a zinc dialkyldithiophosphate, an oxidation inhibitor, and an ashless dithiocarbamate for improving the detergency and oxidation stability at elevated temperatures in a lubricating oil composition for gas engines comprising a major amount of a base oil of lubricating viscosity and an effective amount of a metal-containing detergent, a boron-containing alkenyl- or alkylsuccinimide, a zinc dialkyldithiophosphate, an oxidation inhibitor, and an ashless dithiocarbamate.

[0020] Among other factors, the present invention is based on the surprising discovery that the lubricating oil composition of the present invention provides improved detergency and oxidation stability at elevated temperatures in gas engines. Moreover, the lubricating oil composition of the present invention provides excellent oxidation stability under gaseous nitrogen oxide conditions. Hence, the lubricating oil composition of the present invention is useful in a method of improving the detergency and oxidation stability at elevated temperatures of gas engines. In that method, the lubricating oil composition of the present invention is also used to lubricate gas engines.

DETAILED DESCRIPTION OF THE INVENTION

[0021] As mentioned above, in its broadest embodiment, the present invention involves a lubricating oil composition having improved detergency and oxidation stability at elevated temperatures. Details of the present invention are described herein below.

Base Oil of Lubricating Viscosity

[0022] The base oil of lubricating viscosity may be a mineral base oil, a synthetic base oil, or their mixture preferably having a kinematic viscosity of 2 to 50 mm²/s at 100°C. A mineral base oil employable for the invention can be obtained from crude oil by distillation (under atmospheric or reduced pressure) and purification (e.g., solvent extraction, hydrocracking, solvent dewaxing, hydrogenation refining). Particularly preferred is a highly hydrogenation-refined base oil such as that having a viscosity index of 100 to 150, an aromatic component of 5 wt % or less, a nitrogen content of 50

ppm or less, and a sulfur content of 50 ppm or less.

[0023] The synthetic base oil can be a poly- α -olefin which is produced by polymerization of α -olefin having about 3 to 12 carbon atoms, a dialkyl ester of an alcohol having about 4 to 12 carbon atoms and a dibasic acid (e.g., sebacic acid, azelaic acid, or adipic acid) such as dioctyl sebacate, a polyol ester of 1-trimethylolpropane or pentaerythritol and

[0024] Each mineral oil and synthetic oil can be employed singly. If desired, two kinds of mineral oils as well as two kinds of synthetic oils are employed in combination in optionally determined ratios. Further, if desired, a mineral oil and a synthetic oil can be employed in combination in optionally determined ratios.

Additive Components

[0025] The lubricating oil composition of the present invention contains a small amount (0.1 to 1 wt %, in terms of a sulfate ash content) of a metal-containing detergent. The content of the metal-containing detergent in the lubricating composition can be varied depending upon the nature of the detergent. Generally, the metal-containing detergent is employed in an amount of 0.1 to 5 wt % in terms of an amount of its active ingredient, i.e., a functional ingredient free from a reaction solvent or dilution solvent which is employed in preparing and/or formulating the detergent.

[0026] There are no specific limitations with respect to the metal-containing detergent employable for the lubricating oil composition of the present invention. Examples of suitable metal-containing detergents include metal salicylate, metal phenate, metal sulfonate, or a complex compound of these metal salts. The metal-containing detergent may be of an overbased type, such as that having a total base number (TBN) of 150 to 300 mg KOH/g or higher. A metal-containing detergent having a less TBN or of a neutral type is also employable.

[0027] The metal salicylate is generally an alkali metal salt or an alkaline earth metal salt of salicylic acid which is produced from an alkylphenol wherein the alkyl group has about 8 to 30 carbon atoms via a Kolbe-Schmitt reaction. Examples of suitable alkaline earth metal salts include calcium salt, magnesium salt, or barium salt. Most preferred is calcium salicylate.

[0028] The metal phenate is generally an alkali metal salt or an alkaline earth metal salt of a sulfurized alkylphenol wherein the alkyl group has about 8 to 30 carbon atoms. Examples of suitable alkaline earth metal salts include calcium salt, magnesium salt, or barium salt. Most preferred is a sulfurized calcium phenate.

[0029] The metal sulfonate is generally an alkali metal salt or an alkaline earth metal salt of a mineral sulfonate having a molecular weight of about 400 to 1,000 or the salt of alkylbenzene sulfonic acid. Examples of suitable alkaline earth metal salts include calcium salt, magnesium salt, or barium salt.

[0030] The metal salicylate, metal phenate, and metal sulfonate can be employed singly or in combination. Also employable are a complex compound of a metal phenate and a metal salicylate and a complex compound of a metal phenate and a metal sulfonate. In addition, each of the metal salicylate, metal phenate, and metal sulfonate can be employed in combination with other metal-containing detergents such as an alkaline earth phosphonate and an alkaline earth metal naphthenate. Preferably, the metal-containing detergent contains at least 50 wt % of an alkaline earth metal salicylate, specifically calcium salicylate, having a total base number of 50 to 250 KOH/g.

[0031] In the lubricating oil composition of the present invention, the metal-containing detergent is employed in combination with a boron-containing alkenyl- or alkylsuccinimide. The amount of the boron-containing alkenyl- or alkylsuccinimide varies depending upon the nature, particularly the boron content, of the employed succinimide. Generally, the boron-containing alkenyl- or alkylsuccinimide is employed in an amount of 1 to 15 wt %, in terms of its content of active ingredient (i.e., functional ingredient free from a reaction solvent and a dilution solvent).

[0032] The boron-containing alkenyl- or alkylsuccinimide is an alkenyl- or alkylsuccinimide to which a boron atom is connected. Boron-containing alkenyl- or alkylsuccinimides are known and can be prepared by causing a reaction between succinic anhydride having a high molecular weight alkenyl or alkyl substituent and a polyalkylene polyamine containing an average of about 4 to 10, preferably about 5 to 7, nitrogen atoms (per one molecule), and subjecting the reaction product to post-treatment with boric acid or boric acid derivative. The boron-containing alkenyl or alkylsuccinimide preferably contains 0.1 to 5 wt %, preferably 0.2 to 4 wt %, of boron (in terms of its active ingredient content). The succinic anhydride having a high molecular weight alkenyl or alkyl substituent is preferably obtained by the reaction between polybutene having a number average molecular weight of 1,000 to 2,700 and maleic anhydride.

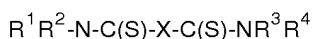
[0033] The lubricating oil composition of the present invention further contains a zinc dialkyldithiophosphate (Zn-DTP) in an amount of 0.01 to 0.1 wt %, in terms of phosphorus content. This phosphorus content range approximately corresponds to 0.05 to 2.0 wt % in terms of an active Zn-DTP ingredient content. The zinc dialkyldithiophosphate preferably has an alkyl group containing about 3 to 18 carbon atoms or an aryl group having an alkyl moiety containing about 3 to 18 carbon atoms. Most preferred is a Zn-DTP having an alkyl group which is derived from a secondary alcohol containing about 3 to 18 carbon atoms or a mixture of a primary alcohol containing about 3 to 18 carbon atoms and a secondary alcohol containing about 3 to 18 carbon atoms. The incorporation of an alkyl group from a secondary alcohol is preferred because it is more effective in reducing wear.

[0034] The lubricating oil composition of the present invention further contains a phenol oxidation inhibitor (hindered phenol oxidation inhibitor) or an amine oxidation inhibitor (diarylamine oxidation inhibitor) in an amount of 0.1 to 5.0 wt %, preferably 0.1 to 3.0 wt %. Examples of suitable hindered phenol oxidation inhibitors include 2,6-di-t-butyl-p-cresol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-methylenebis(6-t-butyl-o-cresol), 4,4'-isopropylene bis(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-thiobis(2-methyl-6-t-butylphenol), 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate], and octyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate.

[0035] Examples of suitable diarylamine oxidation inhibitors include alkylldiphenyl amine (in which the alkyl moiety is a mixture of alkyl groups having about 4 to 9 carbon atoms), p,p'-dioctyldiphenylamine, phenyl- α -naphthylamine, phenyl β -naphthylamine, alkylated α -naphthylamine, and alkylated phenyl- α -naphthylamine. Each hindered phenol oxidation inhibitor and diarylamine oxidation inhibitor can be employed singly or in combination, if desired.

[0036] The lubricating oil composition of the present invention further contains an ashless (which means "metal element free") dithiocarbamate compound in an amount of 0.1 to 5 wt %.

[0037] The ashless dithiocarbamate having the following formula is preferably employed in the lubricating oil composition of the present invention:



wherein each of R^1 , R^2 , R^3 , and R^4 independently is an alkyl group having about 1 to 18 carbon atoms and X is S, S-S, S-CH₂-S, S-CH₂CH₂-S, S-CH₂CH₂CH₂-S, or S-CH₂CH(CH₃)-S.

[0038] The ashless dithiocarbamate compound of the above-mentioned formula is an additive for rubber (i.e., vulcanizing agent) or an additive for gear oils and turbine oils. The alkyl group can be a straight-chain alkyl group or a branched-chain alkyl group. Examples include methyl, ethyl, propyl, n-butyl, isobutyl, pentyl, isopentyl, heptyl, octyl, 2-ethylhexyl, nonyl, decyl, and dodecyl. Preferred are alkyl groups having about 1 to 10 carbon atoms.

[0039] Examples of suitable ashless dithiocarbamate compounds include methylene bis(dibutylthiocarbamate), bis(dimethylthiocarbamoyl)monosulfide, bis(dimethylthiocarbamoyl)disulfide, bis(dibutylthiocarbamoyl)disulfide, bis(di-amythiocarbamoyl)disulfide, and bis(dioctylthiocarbamoyl)disulfide. Each of the compounds can be incorporated singly or in combination in an amount of 0.1 to 5 wt % in the lubrication oil composition of the present invention. The preferred ashless dithiocarbamate is methylene bis(dibutylthiocarbamate).

[0040] The lubricating oil composition of the present invention can further contain a variety of auxiliary additives in addition to the above-described additive components. Examples of the auxiliary additives include extreme pressure agents, corrosion inhibitors, rust inhibitors, friction modifiers, anti-foaming agents, viscosity index improvers and pour point depressants. Also employable are anti-wear agents and multi-functional additives (e.g., an organic molybdenum compound such as molybdenum dithiophosphate). As the viscosity improver, polyalkyl methacrylate, ethylene-propylene copolymer, styrene-butadiene copolymer, or polyisobutylene is generally employed. Otherwise, a dispersion-type or multi-functional viscosity index improver can be employed. The viscosity index improver can be used singly or in combination of various types. The amount of a viscosity index improver in the lubricating oil can vary depending upon the viscosity desired for the target engine oil. Generally, the viscosity index improver can be incorporated into the engine oil in an amount of 0.5 to 20 wt %.

[0041] The lubricating oil composition of the present invention has a sulfated ash content in the amount of 0.1 to 1 wt %, a phosphorus content in the amount of 0.01 to 0.1 wt %, and a boron content in the amount of 0.01 to 0.2 wt %.

EXAMPLES

[0042] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the Examples are provided to illustrate the present invention, they are not intended to limit it. This application is intended to cover those various changes and substitutions that may be made by those skilled in the art without departing from the spirit and scope of the appended claims.

Example 1

[0043] Samples of the lubricating oil composition of the present invention in which essential additives and various auxiliary additives were incorporated and comparative lubricating oil samples in which at least one of the essential additives was not incorporated were prepared, and evaluated for detergency and oxidation stability at elevated temperatures.

[0044] The high temperature detergency was evaluated by a hot tube test. In the hot tube test, a glass tube (inner diameter: 2 mm) was set vertically to the heater block. A test oil and air were sent to the glass tube from its bottom at

EP 1 104 800 A2

rates of 0.31 cc/hr and 10 cc/min, respectively. The glass tube was kept at the predetermined temperature (i.e., test temperature) for 16 hours. After the heating, the conditions of deposit produced on the inner wall of the glass tube was evaluated based on one to ten points marks.

[0045] The oxidation stability was evaluated at 165.5°C for 96 hours by the oxidation stability test of lubricating oils for internal combustion engines according to JIS K 2514. In the evaluation, characteristics of the test oil before the test were compared with the characteristics of the test oil after the test.

[0046] In the examples, the additive components are:

(1) Ashless dispersant-1: a reaction product (nitrogen content: 1.5 wt %, boron content: 0.5 wt %) of a bis-type succinimide (derived from polybutene having a number average molecular weight of about 1,300 and boric acid)

(2) Ashless dispersant-2: a bis-type succinimide (nitrogen content: 1.5 wt %) derived from polybutene having a number average molecular weight of about 1,300.

(3) Metal detergent-1: calcium salicylate (TBN: 170 mg KOH/g)

(4) Metal detergent-2: calcium sulfonate (TBN: 20 mg KOH/g)

(5) Zn-DTP: zinc dialkyldithiophosphate (phosphorus content: 7.4 wt %) derived from primary alcohol having about 4 to 10 carbon atoms

(6) Diarylamine-1: dialkyldiphenylamine having a mixed alkyl moieties (butyl and octyl)

(7) Diarylamine-2: phenyl- α -naphthylamine

(8) Hindered phenol: 4,4'-methylene bis(2,6-di-*t*-butylphenol)

(9) Dithiocarbamate: methylene bis(dibutyldithiocarbamate)

(10) Auxiliary additives: a mixture of rust inhibitor, anti-oxidant, metal deactivator, anti-foaming agent, etc.

(11) Base oil: 500 neutral oil (viscosity index: 100)

[0047] The formulations of test oils are set forth below.

TABLE 1

Test Oils, wt % ^a								
	INVENTION				COMPARATIVE			
	1	2	3	4	A	B	C	D
Ashless dispersant-1	6.0	6.0	6.0	6.0	-	-	6.0	6.0
Ashless dispersant-2	-	-	-	-	6.0	6.0	-	-
Metal detergent-1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1
Metal detergent-2	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Zn-DTP	0.33	0.33	0.33	0.33	0.33	0.33	0.33	0.33
Diarylamine-1	1.0	0.75	1.0	-	1.0	0.75	1.5	-
Diarylamine-2	-	-	0.1	-	-	-	-	-
Hindered phenol	-	-	-	0.75	-	-	-	-
Dithiocarbamate	0.5	0.75	0.5	0.75	0.5	0.75	-	1.5
Auxiliary Additives	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

^aSAE 30 viscosity grade lubricating oil, total sulfated ash 0.48 wt %, total phosphorus content 0.024 wt %.

EP 1 104 800 A2

TABLE 1 (continued)

Test Oils, wt % ^a								
	INVENTION				COMPARATIVE			
	1	2	3	4	A	B	C	D
Base oil	89.52	89.52	89.42	89.52	89.52	89.52	89.52	89.52

^aSAE 30 viscosity grade lubricating oil, total sulfated ash 0.48 wt %, total phosphorus content 0.024 wt %.

[0048] The results of the evaluations are set forth in the following Table 2.

TABLE 2

	Test Oil				Test Oil			
	(Invention)				(Comparative)			
	1	2	3	4	A	B	C	D
Oxidation stability								
Viscosity increase (40°C, %)								
	6	3	6	2	16	11	43	3
Total acid value increase (mg KOH/g)								
	1.51	1.06	1.38	1.29	4.20	2.01	6.04	1.83
TBN retention ratio (hydrochloric acid method, %)								
	10.7	15.2	11.8	20.3	0	7.2	7.4	7.7
High temperature detergency								
Hot tube test (maximum: 10 points)								
(290°C)	8.5	8.5	8.5	7.5	2.5	2.5	9.0	3.5
(300°C)	5.5	4.0	6.0	5.5	0	0	8	2.0

[0049] From the results set forth in Table 2, the test oils of the present invention show both high oxidation stability and high detergency at elevated temperatures for a long period of time. In contrast, the comparative test oils, i.e., A, B, C, and D, in which a borated succinimide derivative, a diarylamine, a phenol compound, or dithiocarbamate is not present are apparently unsatisfactory in detergency and oxidation stability at elevated temperatures.

Example 2

[0050] Test Oil 2 and Test Oil 4 of the present invention were evaluated for resistance to NO_x oxidation.

[0051] The evaluation test was performed by the following procedures.

[0052] In 40 mL of the test oil are placed a iron piece and a copper piece (defined in Oxidation Stability Test, JIS K 2514). The test is then kept at 140°C. Into the heated test oil are introduced a nitrogen gas containing 0.8 vol.% of NO_x gas and a wet air (which is produced by passing air through water) at rates of 5.7 U_{hr} and 15 U_{hr}, respectively. The introduction of these gasses into the heated test oil is continued for 96 hours, and the characteristics of the test oil prior to the test and those of the test oil after the test are compared. The results are set forth in Table 3.

TABLE 3

	Test Oil 2	Test Oil 4
Viscosity increase (40°C, %)	40	22
Total Acid Number (TAN) increase (mg KOH/g)	3.36	2.60
TBN retention (HCl method, %)	0	1.2

[0053] The results in Table 3 indicate that the test oils for the present invention show satisfactory resistance to NO_x oxidation. It is further noted that Test Oil 4 utilizing a hindered phenol is superior in resistance to NO₂ oxidation than Test Oil 2 utilizing diarylamine.

Claims

1. A lubricating oil composition for internal combustion engines comprising:

- a) a major amount of a base oil of lubricating viscosity,
- b) a metal-containing detergent in an amount of 0.1 to 1 wt % in terms of its sulfated ash content,
- c) a boron-containing alkenyl- or alkylsuccinimide in an amount of 1.0 to 15 wt % in terms of its active ingredient,
- d) a zinc dialkyldithiophosphate in an amount of 0.01 to 0.1 wt % in terms of its phosphorus content,
- e) an oxidation inhibitor in an amount of 0.1 to 5 wt % in terms of its active ingredient, and
- f) an ashless dithiocarbamate in an amount of 0.1 to 5 wt % in terms of its active ingredient.

2. A lubricating oil composition according to Claim 1, wherein said lubricating oil composition has a sulfated ash content in an amount of 0.1 to 1 wt %.

3. A lubricating oil composition according to Claim 1, wherein said lubricating oil composition has a phosphorus content in an amount of 0.01 to 0.1 wt %.

4. A lubricating oil composition according to Claim 1, wherein said metal-containing detergent is an alkaline earth metal salicylate.

5. A lubricating oil composition according to Claim 4, wherein said alkaline earth metal salicylate has a total base number of 50 to 250 mg KOH/g.

6. A lubricating oil composition according to Claim 1, wherein said oxidation inhibitor is a diarylamine or hindered phenol.

7. A lubricating oil composition according to Claim 1, wherein said ashless dithiocarbamate is methylene bis(dibutyldithiocarbamate).

8. A lubricating oil composition according to Claim 1, wherein said lubricating oil composition having a boron content of 0.01 to 0.2 wt %.

9. A method of producing a gas engine lubricating oil composition comprising blending the following components together:

- a) a major amount of a base oil of lubricating viscosity,
- b) a metal-containing detergent in an amount of 0.1 to 1 wt % in terms of its sulfated ash content,
- c) a boron-containing alkenyl- or alkyl-succinimide in an amount of 1.0 to 15 wt % in terms of its active ingredient,
- d) a zinc dialkyldithiophosphate in an amount of 0.01 to 0.1 wt % in terms of its phosphorus content,
- e) an oxidation inhibitor in an amount of 0.1 to 5 wt % in terms of its active ingredient, and
- f) an ashless dithiocarbamate in an amount of 0.1 to 5 wt % in terms of its active ingredient.

10. A method of improving the detergency and oxidation stability at elevated temperatures of a gas engine, said method comprising lubricating said gas engine with the lubricating oil composition of Claim 1.

11. A method for lubricating a gas engine with the lubricating oil composition according to Claim 1.